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A PROCESS AND A PLANT FOR RECYCLING CARBON DIOXIDE EMISSIONS FROM POWER PLANTS INTO USEFUL CARBONATED SPECIES

FIELD OF THE INVENTION

The present invention relates generally to processes and apparatuses used for energy production in fossil-fuel power plants. More particularly, it concerns a process and a plant for the sequestration of carbon dioxide emissions emanating from fossil-fuel power plants, and for the production of useful carbonated species.

BACKGROUND OF THE INVENTION

Fossil-fuel power plants produce the main part of the energy actually consumed worldwide. Energy is generated from the combustion of fossil-fuels such as coal, natural gas and fuel oil. The use of biomass to fuel the power plant is also within the scope of this invention. Main exhaust gases formed from such processes may be CO_2, SO_2 and NO_x depending on the nature of the fuel used. Treatment systems are already available for reducing SO_2 and NO_x emissions. However to date, CO_2 emissions from fossil-fuel power plants are generally not contained or reduced. These CO_2 emissions thus contribute to increase the atmospheric concentration of CO_2, the most important greenhouse gas. It is known that such an increase in greenhouse gases causes climate changes which could lead to various environmental problems, such as an increase in violent weather events, significant temperature warming in specific areas, changes in the precipitation pattern trends and a rise of ocean level.

Moreover, in the next century, a significant increase of carbon dioxide concentrations is expected, unless energy production systems reduce their emissions into the atmosphere. Carbon sequestration consisting of carbon capture, separation and storage or reuse represents potent ways to stabilize and eventually reduce concentration of atmospheric CO_2.

Several technologies, based on carbon sequestration, are being studied by academic and industrial groups. These are: transformation by algae, sequestration in oceans, storage in depleted oil and natural gas wells and dissolution of pressurized CO_2 in water tables. CO_2 can also be transformed into more geologically stable forms, such as calcium carbonate.

Transformation of CO_2 with algae involves the use of algal photosynthesis. The gas emitted by power stations is thus directly introduced in basins located nearby. The selected algae must therefore support these environments with harsh conditions. The algae produced could be dried up and used as fuel to supply the power station. This approach reduces the required fuel to supply power, but does not eliminate CO_2 production completely.

Sequestration in oceans consists in pumping the carbon dioxide to be disposed of to depths of 1,000 metres below sea level. The technique is based on the fact that CO_2 possesses a higher density than water. It is believed that CO_2 will sink to the bottom of oceans where lakes of liquid carbon dioxide will be formed. However, as yet, the environmental impact of this technology has not been demonstrated (US 6,475,460). Another way is to bring carbon dioxide and seawater or fresh water into contact to form carbon dioxide hydrate and sinking it in the seawater, fresh water or geological formation under conditions for the stability of carbon dioxide hydrate (CA 2,030,391, patent application US 2003/0055117, patent application US 2003/0017088; US 6,254,667).

Oil and natural gas wells are capable of supporting enormous pressures without leakage. They are therefore an ideal location for the storage of compressed CO_2 (patent application CA 2,320,216; US 6,598,398; US 6,389,814; US 6,170,264). In the petroleum industry, the injection of CO_2 in wells to enhance oil recovery is a widely used technique. However, this method only constitutes a temporary storage, since in the medium

term, the displacements of the earth crust are capable of bringing about a release of CO_2. Moreover, although there are hundreds of depleted sites around the world, their total capacity is after all limited, and there is an obligation to land case the geological formations involved.

The deep water tables are distributed throughout the globe. They generally include salt water and are separated from the surface water tables which constitute the drinking water supplies. The water contained in these natural reservoirs can dissolve the pressurized CO_2 and even disperse it in the geological formations. However, the implementation of this technology must always imply a strong concern regarding the proximity of the water tables with the CO_2 emission sources.

CO_2 sequestration in solid carbonates and/or bicarbonates has already been reported in Lee et al. (US 6,447,437). However, CO_2 chemical transformation into bicarbonate fertilizer requires methane, hydrogen and nitrogen. Kato et al. (US 6,270,731) reported CO_2 sequestration into carbon powder. However, methane and hydrogen are required. Shibata et al. (US 5,455,013) reported CO_2 sequestration into $CaCO_3$. However, the chemical process enables CO_2 sequestration into $CaCO_3$ only. Other carbonates cannot be obtained.

Although some solutions have been proposed in the past for reducing CO_2 emissions in general, few of them have shown to be efficient or commercially viable for different reasons. Moreover, a very few, if not none, of the solutions proposed specifically apply to CO_2 emissions from fossil-fuel power plants. Thus, there is still a need for a solution for reducing those CO_2 emissions from fossil-fuel power plants. With the general concern throughout the world with respect to the urgency of finding a solution to the problem of emissions of greenhouse gases, this need is even more obvious.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a process and a fossil-fuel power plant that satisfy the above mentioned need.

This process is characterized in that it comprises a step where the CO_2 emissions from the fossil-fuel power plant are transformed by means of a biological process into different useful carbonated species, such as calcium carbonate, a geological natural product.

More particularly, in accordance with the present invention, the above object is achieved with a process for recycling carbon dioxide emissions from a fossil-fuel power plant into useful carbonated species, which process primarily comprises the steps of: a) combustion of a fossil fuel, thereby generating heat and a hot exhaust gas containing CO_2; and b) converting the heat into energy. The process is characterized in that it further comprises the steps of: c) cooling the exhaust gas; and d) biologically transforming at least a portion of the CO_2 contained in the cooled exhaust gas into carbonated species, thereby obtaining a low CO_2 exhaust gas and producing useful carbonated species. The low CO_2 exhaust gas obtained in step d) can be released in the atmosphere without increasing the problem of greenhouse effect.

By biological process, it is meant a process involving the activity of living organisms.

More particularly, the step d) of biologically transforming the CO_2 defined above preferably comprises the steps of: catalyzing the hydration of at least a portion of the CO_2 contained in the exhaust gas, and producing a solution containing hydrogen ions and carbonate ions. Then, metal ions are added to the solution, and the pH is adjusted to precipitate a carbonate of that metal. These metal ions are preferably selected from the group consisting of calcium, barium, magnesium and sodium ions. More preferably, Ca^{++} is used and the carbonate obtained is $CaCO_3$.

The hydration is catalyzed by a biocatalyst capable of catalyzing the hydration of dissolved CO_2 into hydrogen ions and bicarbonate ions. More preferably, the biocatalyst is selected from the group consisting of enzyme, cellular organelle, mammal cells and vegetal cells. Most preferably, the biocatalyst is the enzyme carbonic anhydrase or an analogue thereof.

CO_2 transformation takes place inside a bioreactor and is performed by a biocatalyst which accelerates the transformation of CO_2 into bicarbonate in an aqueous environment. The bicarbonate can then be precipitated into a stable solid product.

This invention thus proposes the integration of a CO_2 transformation process into a fossil-fuel power plant in order to produce bicarbonate species which are useful by-products, and thereby reducing at the same time the CO_2 emissions. This CO_2 transformation process is based on a biological reactor which enables CO_2 transformation into bicarbonate in an aqueous environment. The CO_2 is then precipitated into a stable solid product, safe for the environment. As can be appreciated, in the present invention, only water, a biocatalyst and a cation source are required for carbon dioxide sequestration.

In accordance with a preferred aspect of the invention, step d) of biologically transforming the CO_2 comprises the step of: feeding liquid H_2O and at least a portion of the exhaust gas, preferably all, into a bioreactor containing therein a reaction chamber filled with the biocatalyst. The biocatalyst is optionally immobilized on solid supports packing the bioreactor or in suspension in a liquid phase. In that latter case, the biocatalyst may be either free in the aqueous liquid phase, immobilized on solid supports or entrapped inside a solid matrix.

The present invention also provides a power plant for producing energy from fossil fuel, and recycling carbon dioxide emissions into carbonated species. The plant comprises a combustion unit for burning fossil fuel,

thereby producing heat and an exhaust gas containing CO_2; and conventional means for converting the heat into energy. The plant is characterized in that it further comprises: means for cooling the exhaust gas; and biological means for biologically transforming at least a portion of the CO_2 from the cooled exhaust gas into hydrogen ions and carbonate ions, and means for precipitating carbonated species.

The biological means preferably comprises a bioreactor including a reaction chamber filled with a biocatalyst capable of catalyzing the hydration of dissolved CO_2 into hydrogen ions and bicarbonate ions. The reaction chamber preferably comprises:

- a liquid inlet for receiving an aqueous liquid;
- a gas inlet for receiving the cooled exhaust gas to be treated;
- a gas outlet for releasing a low CO_2 gas; and
- a liquid outlet for releasing a solution containing carbonate ions.

Also preferably, the precipitation means comprises a precipitation vessel, wherein the bicarbonate ions can react with metal ions and precipitate a carbonate of that metal.

GENERAL DESCRIPTION OF THE INVENTION

CO_2 production in a fossil fuel power plant

CO_2 is produced during combustion of fossil fuels such as coal, natural gas or fuel oil (Equation 1). For the purpose of the present invention, fossil-fuel power plant is also directed to power plants using biomass as the fuel. In the case of a coal power plant, the heat released during this combustion is used to heat water and produce steam which then passes through steam turbines coupled to electric alternators leading to electricity generation. In

the case of a natural gas power plant, the fuel is burned directly in gas turbines coupled to electric alternators.

$$C_xH_y + (x+y/4)\,O_2 \xrightarrow{\Delta} x\,CO_2 + y/2\,H_2O \qquad \text{Equation 1}$$

Other gases may also be produced by combustion, namely SO_2 and NO_x given the original sulphur and nitrogen content of the used fuel. These other gases are encountered mainly in coal power plants.

Flue gas exhausting from combustion chambers and containing CO_2 is discharged directly to the atmosphere. In the context of this invention, CO_2 emissions are treated and reduced by a biological process.

In the case of coal power plants, flue gas has first to be cooled in order to have a temperature that does not lead to the denaturizing (free and/or immobilized) of the biocatalyst. Gas cooling is obtained with any type of heat exchanging device, and the recovered energy is preferably used to increase the process efficiency. The heat could, for example, be used to pre-heat the air required for combustion, or to supply energy for additional turbines. The gas is then preferably treated to remove excess ash, SO_2 and NO_x, in order that the gas be of optimum quality for the biological process. Ash can be removed using units such as electrostatic precipitators and fabric filters. SO_2 can be removed using scrubber units and NO_x using burners or catalytic systems. leading to the conversion of NO_x to N_2 and H_2O. These units, which are used to remove ash, SO_2 or NO_x, are already known in prior art and do not need further description.

CO_2 transformation in a biological process

Gas phase containing CO_2 with appropriate level of ash, SO_2, NO_x and at appropriate temperature and pressure, is then fed to the biological process, enabling CO_2 transformation into bicarbonate and hydrogen ions, and then to useful carbonated species. This biological process is preferably performed in a biological reactor where CO_2 transformation

takes place. This transformation is catalyzed by a biocatalyst accelerating CO_2 transformation. The biocatalyst is a biological entity which can transform a substrate in one or more products. The biocatalyst is preferably an enzyme, a cellular organelle (mitochondrion, membrane, etc.), and animal, vegetal or human cells. More preferably, the biocatalyst is the enzyme carbonic anhydrase but may be any biological catalyst enabling CO_2 transformation. CO_2 transformation reaction is the following:

$$CO_2 + H_2O \overset{enzyme}{\rightleftharpoons} HCO_3^- + H^+ \qquad \text{Equation 2}$$

This reaction is natural. It is at the basis of CO_2 transportation and removal phenomenon in the human body and in most living beings.

The biological catalyst may be free or immobilized inside the biological reactor. An example of a bioreactor which could be used for biological transformation of CO_2 is described in "Process and Apparatus for the Treatment of Carbon Dioxide with Carbonic Anhydrase" (Blais et al.)(CA 2,291,785; WO98/55210). In this process, carbonic anhydrase is immobilized onto solid supports. Solid supports can be made of various organic and inorganic material and have shapes proper to packed columns. The gas phase containing CO_2 enters at the bottom of the packed column and the liquid phase enters at the top of the column. Both phases flow counter currently and close contact of liquid and gas phases is promoted by a solid support having immobilized enzymes on its surface. Gaseous CO_2 is then transferred to the liquid phase where it dissolves and then is transformed according to Equation 2. The liquid flows in and out of the column and is treated for precipitating the bicarbonate ions produced by the bioreaction.

Another biological reactor with free and/or immobilized enzymes for CO_2 transformation into bicarbonate is the following.

The bioreactor consists of a chamber containing biocatalyst particles. The gas to be treated enters at the bottom of the chamber. A diffusion system is responsible for the uniform distribution of the gas phase at the bottom of the chamber and is designed for minimum bubble diameter. These conditions are required to optimize gas-liquid contact. An agitation device (magnetic or mechanical) can also be used to assure uniform biocatalyst distribution. Liquid phase enables gas dissolution and thus the biocatalytic reaction. In this process, the biocatalyst (preferably carbonic anhydrase, but may be any biological catalyst) is free in the liquid phase and/or immobilized onto a solid support and/or entrapped inside a solid matrix. These particles are moving freely in the liquid and are prevented from exiting the chamber by a membrane or filter. The liquid flows in and out of the chamber and is treated for precipitation of the bicarbonate ions produced by the bioreaction.

As mentioned, bicarbonate ions produced in these two types of bioreactors are preferably precipitated and finally sequestrated. This precipitation is obtained by combining bicarbonate ions to cations. Cations used are preferably calcium, barium, magnesium, sodium or any cation that could lead to the formation of carbonate or bicarbonate salts. As shown in Figure 2, a potential source of cations is the reagent solution coming out of the SO_2 treatment unit. Bicarbonate ions can also be used directly in other chemical or biological processes.

In summary, CO_2 is to be transformed, for example into calcium carbonate, in the biological process, according to the following reactions:

$$CO_2 \text{ dissolved} + H_2O \Rightarrow H^+ + HCO_3^-$$

$$HCO_3^- \Rightarrow H^+ + CO_3^{2-}$$

$$CO_3^{2-} + Ca^{2+} \Rightarrow CaCO_3$$

The coupling of the biological process for CO_2 removal and transformation to a fossil-fuel power plant leads to a reduction of CO_2 emissions into the atmosphere and an increase energy efficiency of the plant. Furthermore, the required cooling of the flue gas enabling proper operation of the bioreactor is coupled with energy recovery systems that produce additional power output for the power plant.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a flow sheet of a preferred embodiment of the process according to the invention, in the context of power plant processes.

Figure 2 is a flow sheet of a further preferred embodiment of the process according to the invention, in the context of power plant processes.

MORE DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Figure 1 shows a flow sheet where a biological process is integrated to energy generation processes.

In this diagram, the nature of the fossil fuel (10), either coal (12) or natural gas (14), used to power the plant leads to two different branches.

In the case of coal (12), the fuel is burned in a combustion chamber (16); the heat (17) is used to produce steam from water in a heat recovery steam generator system (18). The steam propels turbines and alternators (20) producing electric power. The flue gas (22) exiting the combustion chamber (16) is treated to remove ash, NO_x and/or SO_2 (23). In the current configuration of power plants, the gas is finally exhausted by a stack (24).

In the context of this invention, the gas (26) is not exhausted at this stage, but rather sent to additional heat exchangers and energy recovery systems (28) to cool it down to an adequate temperature for the biological process. Energy is produced by this step. The cooled gas (30) is then treated in a gas treatment unit (32) to remove additional contaminants that may be

harmful to the biological process, and finally, CO_2 is removed by the bioreactor (34) and the low CO_2 gas (36) is blown to the atmosphere.

In the case of natural gas (14), the fuel (14) is burned directly in the turbine (38), and the intermediary step of steam production is not present in the main power production stage, although it may be used in subsequent heat recovery stages. The rest of the process is analog to that of the left branch (coal).

Figure 2 is a flow sheet schematically showing the integration of the biological process (32) to a SO_2 treatment unit (40).

This diagram shows the cross-linking that may be performed between the biological process, which produces carbonate and/or bicarbonate ions (33), and the SO_2 treatment unit (40) present in the current power plant process. To remove SO_2 from the flue gas (42), a reagent solution (44) is required. An analog solution is also required for the biological process (32). This solution (44), readily available from either sub-processes, may be used in closed loop for both processes.

Experimental results

The feasibility of treating flue gas from power plant by a biological process has been demonstrated. The lab scale biological process enabled CO_2 absorption and its transformation into $CaCO_3$ .The biological process was performed with a 3 operation units each comprising a 3L-bioreactor containing 2 L of packing material with immobilized carbonic anhydrase for CO_2 absorption. The units also included two ion exchange columns required for recovering and concentrating the bicarbonate ions and a precipitation and sedimentation vessel for formation and recovery of solid $CaCO_3$. The bioreactor used was similar to the one described in "Process and Apparatus for the Treatment of Carbon Dioxide with Carbonic Anhydrase" (Blais et al.)(CA 2,291,785; WO98/55210), and was operated at room temperature and atmospheric pressure. Gas phases with CO_2

concentrations ranging from 0.5 to 12% were efficiently treated with the bioreactor. CO_2 removal rate ranged from 1,47 x 10^{-4} to 4,5 x 10^{-3} mol CO_2/min. Bicarbonate ions produced were recovered and concentrated in ion exchange columns. The removal of ions enabled the recycling of the CO_2 absorbent used in the bioreactor. A carbonate/bicarbonate rich solution was obtained following regeneration of ion exchangers. A calcium source, $CaCl_2$ was added to the bicarbonate/carbonate rich solution, conducting to the formation of precipitated calcium carbonate. A carbon mass balance indicated that carbon dioxide removed from the gas was recovered as precipitated $CaCO_3$.

These results indicate that the biological process can be used to manage CO_2 emissions from power plants. Moreover, valuable products such as $CaCO_3$ are produced.

Although the present invention has been explained hereinabove by way of preferred embodiments thereof, it should be understood that the invention is not limited to these precise embodiments and that various changes and modifications may be effected therein without departing from the scope or spirit of the invention.